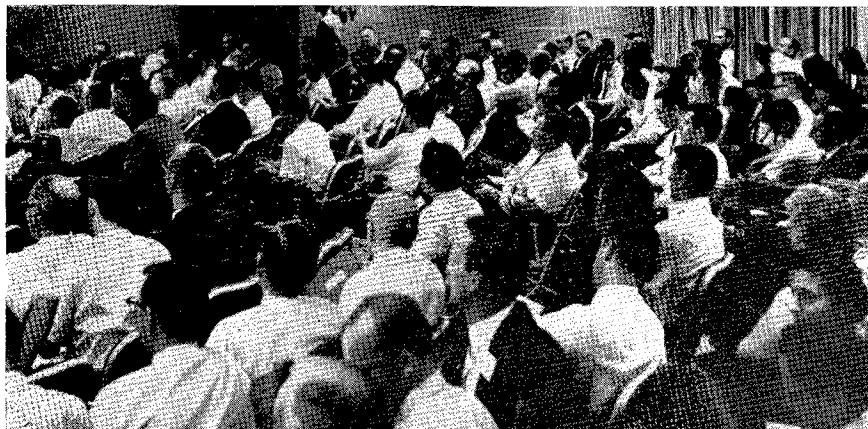


1963 Short Course Draws Record Attendance to Princeton Campus

NOVEMBER ISSUE
TO CARRY
LECTURE SERIES



As a prelude to the November Technical Section of the Journal, which will feature the entire range of papers presented at the 1963 AOCs Short Course, these highlights are offered for those who were unable to attend.

"Advances in Soaps and Detergents" drew a record attendance with a distinct international flavor, June 23-26, with formal registration totalling over 250 for the three-day sessions. Nearly 160 early registrants gathered to enjoy a buffet supper and Sunday evening get-together at the Princeton Inn, site of the Short Course.

In addition to the regular technical sessions, speakers at the Monday and Tuesday dinners were Roy Peet, retired General Manager, Soap and Detergents Association (speaking for E. S. Pattison, who was absent) and G. M. Keller, President, Armour Grocery Products Co. The latter was introduced by Dean of the Faculty, Princeton University, James Douglas Brown.

The official program was opened Monday morning by Eric Jungermann, Program Chairman, with a word of welcome and an expression of thanks to all those who had helped to make the 1963 Short Course such a success.

NEW PRODUCTS AND PROCESSES

Continuous Saponification Processes

A. L. Schulerud, Colgate-Palmolive Co., delivered the opening presentation by giving a brief description of kettle soap boiling, which included a definition of most of the common terms used. He showed schematic diagrams of the DeLaval centrifuge, Sharples, Mecconiche and Mazzonic continuous saponification processes, and pointed out the similarities and differences of each.

Suggestions were given why a continuous system would be favored if new production facilities are needed. However, it was pointed out that it would be difficult to realize a cost saving by switching from the kettle process to any continuous system if certain modernization features were done to the kettle process. He said that with the present low price of glycerin one could eliminate some steps in the process which would not greatly affect the glycerin recovery, but this would be a saving to the soap maker.

Manufacture of Soap from Fatty Acids

A. B. Herrick, Armour & Co., in presenting this talk stated that there are four important steps in making soap from fatty acids. There are, 1) pretreatment, 2) hydrolysis or fat splitting, 3) distillation, and 4) neutralization. A diagram of a Colgate-Emery continuous fat splitter was shown and its operation described. He stated that the hydrolysis or fat splitting stage was the key to making soap from fatty acids. The use of a catalyst, zinc oxide, to increase rate of fat splitting and methods for recovery of zinc was described. The major manufacturing differences between saponification and fat splitting were given with some advantages of fat splitting being in the variety of raw materials which can be used, odor of finished product being better, and smaller amounts of by-products to be utilized.

Continuous Sulfonation Techniques

Sa. J. Silvis, Ing. Mario Ballestra and Co., Milan,

Italy, described Ballestra's continuous sulfonation procedure. He discussed the use of molten sulfur as sulfur trioxide source, and the economics of such a system was also covered. One advantage of using sulfur trioxide in place of oleum is the low level of Na_2SO_4 present in the finished product. It is possible to obtain a finished product containing about 97% active ingredients when using techniques outlined by Dr. Silvis. He described a unique feature of the Ballestra process which uses a free oil (unreacted alkylate) analyzer to insure complete sulfonation in the digester. He discussed the economics of various continuous sulfonation systems.

Tableting of Synthetic Detergents

J. P. Mallee, F. J. Stokes Co., presented the advantages of tableted products. The size, density, and pressure required in making tablets was also discussed. He showed diagrams illustrating various tableting machines and described their operations. He discussed the type of mixing equipment needed to prepare feed material, and the granulation which gave best tablets with proper strength and disintegration properties. Various methods used to handle feed material which did not have good flowability were discussed and methods used to prevent tool sticking and powder buildup were given.

Phosphate Builders for Detergents

Fred McCollough, Victor Chemical Division of Stauffer Chemical Co., presented the chemistry involved in the properties of sodium tripolyphosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate, and sodium metaphosphate. He described the solubility and hydrolysis rate of these polyphosphates as well as the physical chemistry of Type I and Type II sodium tripolyphosphate. The properties of granular sodium tripolyphosphate with regards to density, particle size, frangibility, and absorption capacity were discussed, as well as the use of granular sodium tripolyphosphate in tableted detergents.

Dr. McCollough also discussed the effect of granulation on the strength of the tablet and the effect which Type I or Type II sodium tripolyphosphate has on the rate of disintegration in water.

The New Products session of the Short Course continued, calling the group's attention to a category of detergent "consumers," the naturally occurring bacteria whose job it is to dispose of these products in sewage and ground water. This new consumer has caused the onset of the most revolutionary changes in raw materials and formulations experienced by the detergent industry since its beginning. The concept of biodegradability has served as the stimulus for sweeping research programs that have produced the intended results as well as unsought, but nevertheless valuable routes toward new detergent products.

Alpha-Olefins in the Surfactant Industry

One of the most widely discussed raw materials aimed at by the biodegradable detergent market is *alpha*-olefins, discussed by T. H. Liddicoet, California Research Corp.

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only removes the indicator, the visual sign of stream pollution. Dr. Cohn entered a plea for a more potent program on the part of all concerned, particularly in solving the ground water pollution problem.

The Chemistry of Surfactant Biodegradation

R. D. Swisher, Monsanto Chemical Co., discussed the intermediates formed and the mechanism of biodegradation of detergents. This has been clarified by his recent study of the biodegradation, through co-enzyme A, of straight and branched chain alkylbenzenesulfonates of known structure in river water, monitored by vapor chromatography. Many structural factors influence ease of biodegradation; the position of the sulfo group in the benzene ring, chain length from the sulfo group to the terminal carbon of a straight chain, and the presence of a quaternary carbon at or near the end of the alkyl chain. The latter structure in particular impedes biodegradation because no hydrogen atoms are available for abstraction. Attack can begin at a terminal methyl next to a methylene group and proceed by β -oxidation. Ester or amide straight chain surfactants are easily degraded; branched chain oxyethylated alkylphenols and even branched chain alkyl sulfates are not.

Developments in Products and Processes as They Affect Surface Water and Ground Water Problems

W. A. Kline, Colgate-Palmolive Co., reviewed the research sponsored by the Soap and Detergent Association and the U. S. Public Health Service to understand and solve the problem. Improved sewage treatment might include steps such as the use of activated carbon, purification by foam fractionation, or a deliberate frothing process with recycle of the froth to sewage treatment. New biodegradable detergents may be straight chain ABS, products from α -olefins coming from ethylene, cracked wax, or a chlorination-dehydrochlorination process involving urea adduct formation or the use of molecular sieves, fatty alcohol sulfates, α -sulfo fatty acid esters, or sucrose esters.

Foreign Requirements and Developments as to Detergent Biodegradability

C. A. Houston, Shell Chemical Co., reviewed developments overseas, particularly in the United Kingdom and West Germany where the problem is greater than it is in the United States because of limited water resources. The problem is being solved in England by the voluntary cooperation of industry and government. Trials at Luton with an improved ABS have not completely solved the foam problem but have alleviated it, and large scale tests with "softer" types of ABS, will continue, including also other detergents such as tallow alcohol sulfates. The problem is most acute in West Germany and legislation effective October 1, 1964, states that decomposibility of anionic detergents in washing compositions must be at least 80%, measured in an activated sludge unit using the methylene blue test.

Questions to the panel brought out that improved detergents are not enough, that sewage treatment must be improved, that investigation should precede legislation, and that voluntary action accelerated by competition could solve the problem.

ANALYSES AND PROPERTIES OF DETERGENTS

New Physical Evaluation Techniques

M. E. Ginn, Armour & Co., presented a critical review of recent developments in physical evaluation methods for detergents. He described new and improved methods, with characteristic data for measurement of key detergent prop-

erties: critical micelle concentration, solubilization, emulsifying and dispersing action, and foaming. Latest findings on composition and properties of soil, fabric, and water were discussed; and newly-developed methods for fabric wetting and detergency, including reflectometric and radio-tracer techniques, were presented. Also described were methods for evaluation of hard surface cleaners, including photometric, gravimetric, and radiometric measurements for glass and metals.

Correlation of Detergency with Physico-Chemical Factors

A. M. Mankowich, U. S. Army Coating and Chemical Laboratory, correlated the investigation of hard surface detergency with selected physico-chemical factors in built and unbuilt systems in the practical soil removal range of 90-100%. He showed that the resultant of the combined properties of penetrability, peptization, and wetting—as judged by asphalt soil removal—exhibits synergism on the addition of certain nonionic surfactants to medium pH, aqueous cleaning solutions (ca. pH 12) containing an anionic syndet. He also demonstrated the correlation of soil removal with nonionic surface tension and HLB, and anionic HLB and CMC.

Physical Chemistry of Nonionic Detergents

M. J. Schick, Lever Bros., presented the fact that relatively few papers on the physico-chemical properties of nonionic detergents in aqueous solutions have appeared so far in literature—in contrast to the numerous ones published on ionic detergents.

He described the preparation and characterization of monodisperse alkyl polyoxyethylene alcohols or alkylphenols. He further discussed the determination of the configuration of nonionic detergents at the air/water interface from surface film studies and the factors defining micellar structure in aqueous and aqueous electrolyte solutions. He also described the thermodynamics of micelle formation, solubilization, dispersion, and foaming properties in aqueous solutions of nonionic detergents.

Soil Redeposition

H. B. Trost, Hercules Powder Co., reviewed laboratory methods for evaluating antiredeposition aids, with emphasis on precision, selection of soil, and methods for measuring redeposition effects. He then proposed mechanisms to explain the soil redeposition process and account for the action of water-soluble polymers as antiredeposition aids. And, in light of radioactive tracer studies of adsorption on cotton, the fabric-polymer interaction theory was examined.

Laboratory and scaled-up tests showed the antiredeposition efficiency of water-soluble polymers in a variety of synthetic detergents formulated with neutral and alkaline builders and in alkaline-built soap systems. He concluded by presenting a comparison of the efficiencies of anionic and nonionic polymers on cotton and on washable synthetics, which indicated a dependence on a polymer-fabric relationship.

Recent Advances in Non-Instrumental Analysis of Surface Active Agents

M. J. Rosen, Associate Professor of Chemistry at Brooklyn College and author of a recent book on the systematic analysis of surface active agents, reviewed advances during the last five years. He discussed the use of column, paper, thin layer and ion exchange chromatography as steps associated with the isolation of the active ingredients in a surfactant composition, separation into anionic, cationic, nonionic and ampholytic types, and the identification of the individual surfactant. Chemical methods for detecting characteristic functional groups and the underlying principles and limitations were discussed, illustrated by schematic diagrams. New non-instrumental methods for the quantitative analysis of surface active agents were examined.

Principles and Utility of Nuclear Magnetic Resonance in Structure Determination of Surfactant Chemicals

This paper, by R. R. Irani and M. M. Crutchfield, was presented by Dr. Irani, Monsanto Chemical Co. Although

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An extremely versatile starting material, the *alpha*-olefins should find use in both alkyl and aryl sulfates and sulfonates, cationic derivatives including the quaternary ammonium type germicides, and nonionic surfactants based on ethylene oxide adducts, as well as those comprising long-chain amine oxides. *Alpha*-olefins are to be available in single carbon number cuts. But of much greater interest to the surfactant industry will be various blends of higher molecular weight olefins. The reactive double bond of these products lends itself to a wide variety of reaction products, including halides, carboxylic acids, sulfates, sulfonates, nitro derivatives, amines alcohols, and 1,2-glycols. Application of these products ranges from heavy-duty solids to light-duty liquids, from textile finishing to ore floatation, and from germicides to hard surface cleaning formulations. *Alpha*-olefins are sure to find a significant position in the movement toward new detergent products.

Alcohol Derivatives in Detergent Formulations

T. P. Matson, Continental Oil Co., presented an extensive discussion of long-chain alcohols in their role of raw materials for the detergent industry. In years past, such alcohols have been traditionally prepared by saponification, reduction, or the oxyl process; but within the last year and one-half, entirely straight-chain primary alcohols are now available from Petro Chemical sources. Continental's process for the production of Alfol alcohols has the advantage of being able to produce wide ranges of molecular weight straight-chain alcohols, and therefore makes it necessary to re-evaluate the effect of carbon chain links upon the use properties of such derivatives. It was interesting to note that alcohol sulfates in various combinations of chain links from C₁₃ through C₁₈ could be improved greatly, relative to foam stability by the addition of small percentages of starting alcohol to the built formulation employing the sulfates. A great potential for nonionic products prepared by ethoxylating alcohols lies in the already well-developed fields of light-duty liquids and low-sudsing, heavy-duty formulations. Data indicated that regardless of the chain length of the hydrophobe base, optimum performance properties result from the addition of approximately 62% ethylene oxide (basis molecular weight of the alcohol hydrophobe). The alcohol ether sulfates prepared by sulfation of certain ethoxylates possess the advantage of lending themselves to the use of a wide variety of sulfating agents since ring sulfonation is not a factor. It was shown that alcohol ether sulfates achieve significantly better detergency performance than nonylphenol ether sulfates at the same ethylene oxide content. In foam stability as well as detergency, increase in performance occurs as the ethylene oxide content decreases, or essentially as the alcohol sulfate is approached. Through the availability of wide ranges of hydrophobe molecular weight, these synthetic alcohols promise many routes to new detergent products.

Recent Advances in Fatty Amine Oxides

Part I. Preparative

The literature has been reporting increasing use of certain tertiary fatty amine oxides as effective suds boosters, foam stabilizers, and detergents. D. V. Lake, E. I. duPont de Nemours & Co., discussed the preparative chemistry and properties of dimethyldodecylamine oxide, and described techniques of product isolation and analytical procedures: reaction of a long-chain alcohol with dimethylamine at high temperatures over an alumina catalyst in a tertiary amine, which is converted by treatment with 35% hydrogen peroxide to the desired amine oxide. Although presently finding greatest interest in detergent uses, amine oxides are known for their therapeutic and physiological properties, as well as their capability of serving as a stabilizer in the manufacture of foam rubber. Although the best presently known potential for amine oxides is represented in light-duty liquids of the ether sulfate type, the interesting chemistry of these products will lend themselves greatly to even broader applications.

Part II. Formulation and Uses of Amine Oxides

T. P. Matson, Continental Oil Co., expanded upon the use of amine oxides in light-duty liquids, but pointed out that such products are presently made up of three major types. The first contains dodecylbenzene and ether sulfate; the second utilizes dodecylbenzene and a nonionic; and the third employs an alcohol ether sulfate as the sole active ingredient. Extensive data indicated that of these three types, the latter comprises the best potential for incorporation of an amine oxide. Amine oxide concentrations in the order of 2.5% were shown to provide excellent foam stability. Although certain amine oxides decompose at temperatures above 100C, it was stated to be possible to drum of spray dry finished formulations containing amine oxides without decomposition or loss of foam stability.

Anionic Phosphate Surfactants

R. S. Cooper, Victor Division of The Stauffer Chemical Co., discussed the use of anionic organophosphorus surfactants and stated that such products being marketed by several companies now enjoy a market of approximately 4 million lb per year. These surfactants are now used in or recommended for textile finishing, dry cleaning detergents, foaming agents, emulsion polymerization, floor cleaning concentrates, and other specialty uses. Although none of the anionic phosphate surfactants has ever been used to any appreciable extent in heavy-duty laundry detergents, the interesting and versatile properties of these compounds suggests a potential role in such products. The surface tension of sodium didecyl phosphate solutions, up to a concentration of 200 ppm, is far below that of either sodium dodecylbenzene sulfonate, or sodium tallow sulfate, and is significantly lower than that of an octyl phenol-EO adduct. Performance of sodium didecyl phosphate is also shown to be about 20% more effective than sodium tallow sulfate, nearly twice as effective as sodium lauryl sulfate, and three times as effective as sodium dodecylbenzene sulfonate when used in built detergent. In general, the dialkyl esters possess markedly superior surfactant and detergent properties compared to the monoalkyl esters. This family of detergent products has significant promise as still another candidate for new detergent product development.

SYMPOSIUM ON BIODEGRADABILITY OF DETERGENTS

Because of the great interest in this subject, and the tremendous changes that are involved in a shift from present major types to biodegradable detergents in perhaps two or three years from now, this Tuesday morning symposium was the major attraction of the Short Course. E. S. Pattison of the Soap and Detergent Association, the scheduled Chairman, had been called to Washington in connection with a Senate Committee on detergents and Raymond Liss, Monsanto Chemical Co., took his place. Presentations by four speakers were followed by a lively round table discussion with questions from the audience addressed to the panel members.

The Nation's Water Pollution Problem

M. M. Cohn, editorial director of *Wastes Engineering* and *Water Works Engineering*, brought the subject into focus. He pointed out that in contrast to industrial wastes, which are a back door product, the petroleum industry has been challenged to do something about their front door product, which has been proudly packaged, proudly advertised and proudly used by the housewife. Detergents in water have not been proven to be a health menace; but where foam is, there is sewage; and the removal of foam

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Fun and fellowship played an important role at the buffet supper and dinner meetings held in the Princeton Inn.

the theoretical basis for the phenomenon of nuclear magnetic resonance (NMR) has been understood for 17 years, reliable commercial instrumentation has now developed and NMR can now be considered a practical routine analytical tool. The method is non-destructive and sample volumes as small as 0.007 ml have been used. Quantitative hydrogen NMR measurements can be used for the determination of average structures of surfactant chemicals. Applied to such complicated mixtures of isomers and homologs as the detergent alkylbenzenes, alkylphenols, and ethylene oxide adducts of alkylphenols, the following quantities can be measured with an accuracy of $\pm 2\%$ of the total hydrogen: average length of alkyl chains, average molecular weights, degree and kind of branching in the alkyl chain, the ortho-para distribution of aryl substituents, and the average length of oxyethyl ($-\text{OCH}_2\text{CH}_2-$) chains.

Brightening Agents for Detergents and Related Products

In the closing paper of the Short Course, which still remained very well attended, H. W. Zussman, Geigy Chemical Corp., discussed brightening agents (also called optical bleaches, whitening agents, or fluorescent dyes) as a minor but very important component of detergents. Brightening agents, which may be derivatives and analogs of dye intermediates such as coumarin, diaminostilbene, and dibenzofuran, are colorless dyes substantive to the fabric intended, which in daylight fluorescence in the blue region give the effect of added whiteness. General principles of brightener evaluation were reviewed with emphasis on hue discrimination, consumer preference, and types appropriate to the particular detergent product.

• Industry Items

SWIFT & Co., Chicago, Ill., has announced plans for construction of a multi-million dollar research center on the city's west side, scheduled for completion by early 1965. It will replace their present laboratories in the Union Stock Yards. Plans call for a two-story structure to house 400 scientists, technicians, and supporting staff and facilities for widespread research activities which the company conducts.

UNIVERSAL OIL PRODUCTS Co., Des Plaines, Ill., has created a new subsidiary, UOP Export, Inc., to handle their product export and sales abroad. This expansion follows the growing overseas business of The Trubek Chemical Co. and the more recently acquired Fleuroma division.

ARMOUR & Co., Chicago, Ill., have announced that their Grocery Products Division has been renamed Armour Grocery Products Co., and administrative and sales will move to a downtown location. Balance of the departments will be transferred to the new Dial soap plant near Aurora when it is completed this fall. Soap Research will remain at the old location.

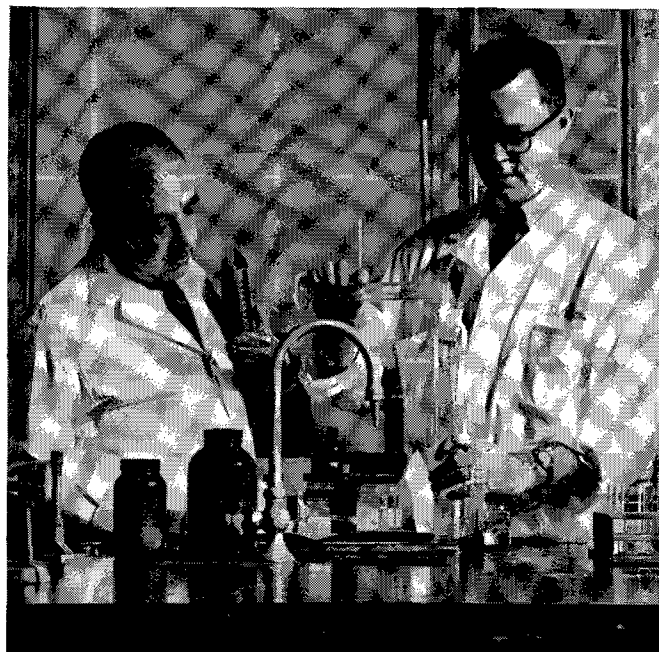
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increased and the Cold Test of the resulting oil is improved. CLARICOL is semi-fluid, easy to handle, economical to use! It is a Food Additive (21 CFR, Subpart D, Section 121-1016).



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